# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

09-132661

(43)Date of publication of application: 20.05.1997

(51)Int.CI.

CO8J 9/06 // CO8L 23:02

(21)Application number: 07-289442

(71)Applicant: HITACHI CHEM CO LTD

(22)Date of filing:

08.11.1995

(72)Inventor: YAMADA MITSUO

OIKAWA SHUNJI MIKAMI YOSHIKATSU

#### (54) PRODUCTION OF FOAM FOR CMP PAD

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a foam used for a CMP pad and having excellent water resistance and consequent durability by forming a mixture comprising a crosslinking agent, a heat-decomposable blowing agent and a polyolefin resin containing an abrasive into a sheet and crosslinking and foaming this sheet.

SOLUTION: A crosslinking agent, a crosslinking aid (A), a heatdecomposable blowing agent (B), an abrasive (C) and a polyolefin resin (D) are melt-kneaded at the decomposition temperature of component B or below, and the resultant mixture is formed into a sheet, This sheet is crosslinked and foamed to form a foam for a CMP(chemical-mechanical polishing) pad. Examples of component D include polypropylene and polyethylene, An example of component A is thutylcumyl peroxide. An example of component B is an organic type such as azodicarbonamide or an inorganic type such as sodium carbonate/citric acid mixture. The composition of a combination of component A with component B is desirably such that cell diameters of several tensum or below can be realized. Component C used is desirably a finely divided silicon oxide abrasive, This foam has excellent water resistance as compared with a conventional urethane foam, so that it can give a CMP pad having durability.

### **LEGAL STATUS**

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **CLAIMS**

### [Claim(s)]

[Claim 1] The manufacture approach of the foam for CMP (Chemical Mechanical Polishing) pads which fabricates the polyolefine system resin constituent containing a cross linking agent and/or a bridge formation assistant, a pyrolysis mold foaming agent, and abrasives in the shape of a sheet, constructs a bridge, foams to this sheet-like moldings, and obtains it. [Claim 2] The manufacture approach of the foam for CMP pads according to claim 1 that polyolefine system resin is characterized by being polypropylene and polyethylene. [Claim 3] The manufacture approach of the foam for CMP pads according to claim 1 that abrasive materials are characterized by being a silica.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

#### **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the foam for CMP pads.

[0002]

[Description of the Prior Art] As for the CMP pad, the foaming polyurethane in which the centrum of the diameter of dozens of micrometers was formed is used conventionally (the monthly SemiconductorWorld1995. May issue, P37). However, generally, since polyurethane is inferior to a water resisting property, a problem is in the endurance of a pad. [0003]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the CMP pad which improved the above-mentioned fault and was excellent in endurance.
[0004]

[Means for Solving the Problem] In this way, according to this invention, the polyolefine system resin constituent containing a cross linking agent and/or a bridge formation assistant, a pyrolysis mold foaming agent, and abrasives is fabricated in the shape of a sheet, and the foam for CMP pads which constructs a bridge, foams to this sheet-like moldings, and is obtained is offered. [0005]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As for the polyolefine system resin used by this invention, resin, such as polypropylene and polyethylene, is used. As polypropylene, polypropylene, such as a gay polypropylene and propylene—ethylene block copolymer, a propylene—ethylene random copolymer, and reactor—polyolefine system thermoplasticity estramer (P. E.R) [it consists of 5 – 45 % of the weight of polypropylene components and 95 – 55 % of the weight of ethylene / propylene copolymerization components], is used. moreover — as polyethylene — low density polyethylene and a line — polyethylene, such as low density polyethylene, medium density polyethylene, and high density polyethylene, is used, and a copolymer with the copolymer of ethylene and alpha olefin, ethylene and other monomers, for example, vinyl acetate, ethyl acrylate, etc. can also be used further. In this invention, these resin can be used as independent or mixture.

[0006] Other various additives can be added to these polyolefin resin in this invention a cross linking agent and/or a bridge formation assistant, a foaming agent, abrasives, and if needed. [0007] As a cross linking agent used for this invention, t-butyl cumyl peroxide, 2, 5 dimethyl -2, 5 di-tert-butyl-peroxide hexane, 2, 5 dimethyl -2, and 5 di-tert-butyl-peroxide hexyne-3 grade can be used, and an addition rate is 0.2 - 5 weight section to the total quantity of a resinous principle, for example. Bridge formation is inadequate in this rate being under the 0.2 weight sections, homogeneity foam is not obtained, if 5 weight sections are exceeded, crosslinking density will go up too much, lug crack and air-bubbles big and rough \*\* happens to foam, and good foam is not obtained.

[0008] As a bridge formation assistant, quinonedioxime, a triaryl TORIMERI rate, trimethylolpropanetrimethacrylate, a trimethylol propane thoria KURI rate, ethylene glycol methacrylate, etc. can be mentioned. Although the addition rate of these bridge formation

assistants can be suitably defined according to a desired bridge formation degree etc., its range of 0.2-5 weight section is usually desirable to the total quantity 100 weight section of a resinous principle.

[0009] The pyrolysis mold foaming agent used by this invention is the compound which decomposes at the time of heating and generates a gas, for example, organic system compounds, such as an AZOJI carvone amide, benzenesulphonyl hydrazide,

dinitrosopentamethylenetetramine, and toluene SUHONIRU hydrazide, and inorganic compounds, such as sodium carbonate / citric-acid mixed stock, are used. The foaming agent with which foam gives the diameter of dozens of micrometer or less air bubbles also especially in these foaming agents is desirable. although the addition of this pyrolysis mold foaming agent can be suitably defined according to desired expansion ratio — the total quantity 100 weight section of a resinous principle — receiving — 2 – 50 weight section — it is preferably used within the limits of 5 – 40 weight section.

[0010] Plasma-CVD-SiO2 film which is a candidate for polish as abrasives used by this invention, If thin film layers (the monthly SemiconductorWorld1995. February issue, P76 reference), such as CVD-TEOS (tetra-ethoxy silane) film and SOG (spin-on glass) film, can be ground according to target extent Although it does not restrict especially, the abrasives which consist of a particle, for example, the abrasives which made the subject the silicon oxide which consists of magnitude of several micrometers – dozens of micrometers, can be used. Although especially the addition to the resin 100 weight section of these abrasives is not limited, generally, it is the 5 – 100 weight section, and is 10 – 80 weight section preferably.

[0011] In this invention, various additives, for example, an antioxidant, an ultraviolet ray absorbent, a modifier, a foam stabilizer, an antistatic agent, a pigment, a filler, etc. can be added if needed.

[0012] melting kneading of polyolefine system resin, a cross linking agent and/or a bridge formation assistant, a foaming agent, abrasives, and the various desired additives is carried out with the decomposition temperature of a cross linking agent, or under the decomposition temperature of a foaming agent, using a Banbury mixer, a roll, an extruder (a monopodium, multiple spindle), etc. as alligation of the above ingredient, finally a press, a dice, etc. are boiled and minded, and it is fabricated in the shape of a sheet.

[0013] In addition, as for the gel molar fraction of the obtained bridge formation foam, it is desirable to adjust the amounts of additives, such as a cross linking agent and a bridge formation assistant, etc. so that it may become 20-80%. Thermal resistance cannot be obtained as too little [ a gel molar fraction ], but an elongation percentage falls that it is conversely excessive, and a poor appearance, such as a lug crack and blistering, generates and is not desirable. Moreover, in this invention, a bridge can be constructed in bridge formation polyolefine system resin using radiations, such as an electron ray, and the above-mentioned bridge formation assistant can be used in this case. Generally the exposure of an electron ray is 1-20Mrad, although the rate of gel of the resin bridge formation section will not limit especially if it becomes 20-80%. It irradiates and is 2-10Mrad preferably. It irradiates.

[0014] The foam by this invention can offer the CMP foam which consists of polyolefine system resin foam which constructs a bridge, foams to the polyolefine system resin constituent containing a cross linking agent and/or a bridge formation assistant, and a pyrolysis mold foaming agent, and is obtained, and is excellent in a water resisting property, as a result is durable. [0015]

[Example] Hereafter, although an example is given and explained about this invention, this invention is not limited to these examples.

[0016] A melt flow rate (MER:230 degree C) 7% of the weight 3g / 10 minutes, [ an example 1 ethylene component ] The ethylene / propylene random copolymer whose melting point is 138 degrees C in the 100 weight sections An AZOJI carvone amide as 5 weight sections and a bridge formation assistant as a foaming agent The trimethylolpropane triacrylate 1 weight section, After having blended so that it might become the 0.5 weight section about IRUGA NOx 1010 as an antioxidant and might become the Aerosil(product made from Japanese Aerosil) 20 weight section with a particle size of 5-20 micrometers as abrasives, and carrying out package kneading

at 155 degrees C using LCM kneading equipment, the pellet with an outer diameter of about 6mm was produced. Incidentally, the extrusion outlet was 65 kg/h. Next, the pellet obtained by this approach was supplied to the hopper of the single screw extruder of 65mm of diameters of a screw, and the dispersibility of resin and a foaming agent fabricated the good sheet by the thickness of about 1mm using the sheet die (passage of the following [ process condition ]). screw: — compression ratio: — 3.0 ratio-of-length-to-diameter: 26 Screw speed: 45rpm Cylinder temperature: C1/C2 / C3/C4; 150/155/155/155 \*\* Adapter temperature: AD;155 degree C dice temperature: D; 155 degrees C, next sheet 2Mrad obtained by this approach After presenting electron beam irradiation, as a result of putting into 230-degree C oven and heating, foam with a good appearance without blistering etc. was obtained by one about 10 times the expansion ratio of this.

[0017] The ethylene / propylene random copolymer whose melting point a melt flow rate (MER:230 degree C) is 138 degrees C for an example 2 ethylene component 7% of the weight for 3g / 10 minutes 80 weight sections, To the polyolefine system resin with which the mixed weight ratio of low density polyethylene/high density polyethylene consists of 70/30 of the polyethylene 30 weight sections An AZOJI carvone amide as 7 weight sections and a bridge formation assistant as a foaming agent The trimethylolpropane triacrylate 1 weight section, After having blended so that it might become the 0.5 weight section about IRUGA NOx 1010 as an antioxidant and might become the Aerosil(product made from Japanese Aerosil) 20 weight section with a particle size of 5-20 micrometers as abrasives, and carrying out package kneading at 155 degrees C using LCM kneading equipment, the pellet with an outer diameter of about 6mm was produced. Incidentally, the extrusion outlet was 70 kg/h. Next, the pellet obtained by this approach was supplied to the hopper of the single screw extruder of 65mm of diameters of a screw, and the dispersibility of resin and a foaming agent fabricated the good sheet by the thickness of about 0.8mm using the sheet die (passage of the following [ process condition ]). screw: -- compression ratio: -- 3.0 ratio-of-length-to-diameter: 26 Screw speed: 45rpm Cylinder temperature : C1/C2 / C3/C4 ; 145/150/150/150 \*\* Adapter temperature : AD;150 degree C dice temperature: D; 150 degrees C, next sheet 2Mrad obtained by this approach After presenting electron beam irradiation, as a result of putting into 230-degree C oven and heating, foam with a good appearance without blistering etc. was obtained by one about 10 times the expansion ratio of this.

[Effect of the Invention] According to this invention, compared with the foam for CMP pads which consists of conventional urethane foam, the CMP pad which is excellent in a water resisting property and is excellent in endurance as a result can be offered.

[Translation done.]

[0018]

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **TECHNICAL FIELD**

[Field of the Invention] This invention relates to the manufacture approach of the foam for CMP pads.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## **PRIOR ART**

[Description of the Prior Art] As for the CMP pad, the foaming polyurethane in which the centrum of the diameter of dozens of micrometers was formed is used conventionally (the monthly SemiconductorWorld1995. May issue, P37). However, generally, since polyurethane is inferior to a water resisting property, a problem is in the endurance of a pad.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **EFFECT OF THE INVENTION**

[Effect of the Invention] According to this invention, compared with the foam for CMP pads which consists of conventional urethane foam, the CMP pad which is excellent in a water resisting property and is excellent in endurance as a result can be offered.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

# **TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the CMP pad which improved the above-mentioned fault and was excellent in endurance.

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

### **MEANS**

[Means for Solving the Problem] In this way, according to this invention, the polyolefine system resin constituent containing a cross linking agent and/or a bridge formation assistant, a pyrolysis mold foaming agent, and abrasives is fabricated in the shape of a sheet, and the foam for CMP pads which constructs a bridge, foams to this sheet-like moldings, and is obtained is offered. [0005]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As for the polyolefine system resin used by this invention, resin, such as polypropylene and polyethylene, is used. As polypropylene, polypropylene, such as a gay polypropylene and propylene-ethylene block copolymer, a propylene-ethylene random copolymer, and reactor-polyolefine system thermoplasticity estramer (P. E.R) [it consists of 5 - 45 % of the weight of polypropylene components and 95 - 55 % of the weight of ethylene / propylene copolymerization components], is used. moreover — as polyethylene — low density polyethylene and a line — polyethylene, such as low density polyethylene, medium density polyethylene, and high density polyethylene, is used, and a copolymer with the copolymer of ethylene and alpha olefin, ethylene and other monomers, for example, vinyl acetate, ethyl acrylate, etc. can also be used further. In this invention, these resin can be used as independent or mixture.

[0006] Other various additives can be added to these polyolefin resin in this invention a cross linking agent and/or a bridge formation assistant, a foaming agent, abrasives, and if needed. [0007] As a cross linking agent used for this invention, t-butyl cumyl peroxide, 2, 5 dimethyl -2, 5 di-tert-butyl-peroxide hexane, 2, 5 dimethyl -2, and 5 di-tert-butyl-peroxide hexyne-3 grade can be used, and an addition rate is 0.2 - 5 weight section to the total quantity of a resinous principle, for example. Bridge formation is inadequate in this rate being under the 0.2 weight sections, homogeneity foam is not obtained, if 5 weight sections are exceeded, crosslinking density will go up too much, lug crack and air-bubbles big and rough \*\* happens to foam, and good foam is not obtained.

[0008] As a bridge formation assistant, quinonedioxime, a triaryl TORIMERI rate, trimethylolpropanetrimethacrylate, a trimethylol propane thoria KURI rate, ethylene glycol methacrylate, etc. can be mentioned. Although the addition rate of these bridge formation assistants can be suitably defined according to a desired bridge formation degree etc., its range of 0.2 – 5 weight section is usually desirable to the total quantity 100 weight section of a resinous principle.

[0009] The pyrolysis mold foaming agent used by this invention is the compound which decomposes at the time of heating and generates a gas, for example, organic system compounds, such as an AZOJI carvone amide, benzenesulphonyl hydrazide,

dinitrosopentamethylenetetramine, and toluene SUHONIRU hydrazide, and inorganic compounds, such as sodium carbonate / citric-acid mixed stock, are used. The foaming agent with which foam gives the diameter of dozens of micrometer or less air bubbles also especially in these foaming agents is desirable. although the addition of this pyrolysis mold foaming agent can be suitably defined according to desired expansion ratio — the total quantity 100 weight section of a resinous principle — receiving — 2 - 50 weight section — it is preferably used within the limits of 5 - 40 weight section.

[0010] Plasma-CVD-SiO2 film which is a candidate for polish as abrasives used by this invention, If thin film layers (the monthly SemiconductorWorld1995. February issue, P76 reference), such as CVD-TEOS (tetra-ethoxy silane) film and SOG (spin-on glass) film, can be ground according to target extent Although it does not restrict especially, the abrasives which consist of a particle, for example, the abrasives which made the subject the silicon oxide which consists of magnitude of several micrometers – dozens of micrometers, can be used. Although especially the addition to the resin 100 weight section of these abrasives is not limited, generally, it is the 5 – 100 weight section, and is 10 – 80 weight section preferably.

[0011] In this invention, various additives, for example, an antioxidant, an ultraviolet ray absorbent, a modifier, a foam stabilizer, an antistatic agent, a pigment, a filler, etc. can be added if needed.

[0012] melting kneading of polyolefine system resin, a cross linking agent and/or a bridge formation assistant, a foaming agent, abrasives, and the various desired additives is carried out with the decomposition temperature of a cross linking agent, or under the decomposition temperature of a foaming agent, using a Banbury mixer, a roll, an extruder (a monopodium, multiple spindle), etc. as alligation of the above ingredient, finally a press, a dice, etc. are boiled and minded, and it is fabricated in the shape of a sheet.

[0013] In addition, as for the gel molar fraction of the obtained bridge formation foam, it is desirable to adjust the amounts of additives, such as a cross linking agent and a bridge formation assistant, etc. so that it may become 20 - 80%. Thermal resistance cannot be obtained as too little [a gel molar fraction], but an elongation percentage falls that it is conversely excessive, and a poor appearance, such as a lug crack and blistering, generates and is not desirable. Moreover, in this invention, a bridge can be constructed in bridge formation polyolefine system resin using radiations, such as an electron ray, and the above-mentioned bridge formation assistant can be used in this case. Generally the exposure of an electron ray is 1 - 20Mrad, although the rate of gel of the resin bridge formation section will not limit especially if it becomes 20 - 80%. It irradiates and is 2 - 10Mrad preferably. It irradiates.

[0014] The foam by this invention can offer the CMP foam which consists of polyolefine system resin foam which constructs a bridge, foams to the polyolefine system resin constituent containing a cross linking agent and/or a bridge formation assistant, and a pyrolysis mold foaming agent, and is obtained, and is excellent in a water resisting property, as a result is durable. [0015]

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

## **EXAMPLE**

[Example] Hereafter, although an example is given and explained about this invention, this invention is not limited to these examples.

[0016] A melt flow rate (MER:230 degree C) 7% of the weight 3g / 10 minutes, [ an example 1 ethylene component ] The ethylene / propylene random copolymer whose melting point is 138 degrees C in the 100 weight sections An AZOJI carvone amide as 5 weight sections and a bridge formation assistant as a foaming agent The trimethylolpropane triacrylate 1 weight section, After having blended so that it might become the 0.5 weight section about IRUGA NOx 1010 as an antioxidant and might become the Aerosil(product made from Japanese Aerosil) 20 weight section with a particle size of 5-20 micrometers as abrasives, and carrying out package kneading at 155 degrees C using LCM kneading equipment, the pellet with an outer diameter of about 6mm was produced. Incidentally, the extrusion outlet was 65 kg/h. Next, the pellet obtained by this approach was supplied to the hopper of the single screw extruder of 65mm of diameters of a screw, and the dispersibility of resin and a foaming agent fabricated the good sheet by the thickness of about 1mm using the sheet die (passage of the following [ process condition ]). screw: -- compression ratio: -- 3.0 ratio-of-length-to-diameter. 26 Screw speed: 45rpm Cylinder temperature: C1/C2 / C3/C4; 150/155/155/155 \*\* Adapter temperature: AD;155 degree C dice temperature: D; 155 degrees C, next sheet 2Mrad obtained by this approach After presenting electron beam irradiation, as a result of putting into 230-degree C oven and heating, foam with a good appearance without blistering etc. was obtained by one about 10 times the expansion ratio of this.

[0017] The ethylene / propylene random copolymer whose melting point a melt flow rate (MER:230 degree C) is 138 degrees C for an example 2 ethylene component 7% of the weight for 3g / 10 minutes 80 weight sections. To the polyolefine system resin with which the mixed weight ratio of low density polyethylene/high density polyethylene consists of 70/30 of the polyethylene 30 weight sections An AZOJI carvone amide as 7 weight sections and a bridge formation assistant as a foaming agent The trimethylolpropane triacrylate 1 weight section, After having blended so that it might become the 0.5 weight section about IRUGA NOx 1010 as an antioxidant and might become the Aerosil(product made from Japanese Aerosil) 20 weight section with a particle size of 5-20 micrometers as abrasives, and carrying out package kneading at 155 degrees C using LCM kneading equipment, the pellet with an outer diameter of about 6mm was produced. Incidentally, the extrusion outlet was 70 kg/h. Next, the pellet obtained by this approach was supplied to the hopper of the single screw extruder of 65mm of diameters of a screw, and the dispersibility of resin and a foaming agent fabricated the good sheet by the thickness of about 0.8mm using the sheet die (passage of the following [ process condition ]). screw: — compression ratio: — 3.0 ratio-of-length-to-diameter: 26 Screw speed :45rpm Cylinder temperature: C1/C2 / C3/C4; 145/150/150/150 \*\* Adapter temperature: AD;150 degree C dice temperature: D; 150 degrees C, next sheet 2Mrad obtained by this approach After presenting electron beam irradiation, as a result of putting into 230-degree C oven and heating, foam with a good appearance without blistering etc. was obtained by one about 10 times the expansion ratio of this.

[0018]

^	10	. 0	••
7	/7	ペー	٠;

JP.09-132661,	A [EXAMP	LE1
---------------	----------	-----